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ATION PAGE

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE 4/22/91	3. REPORT TYPE AND DATES COVERED FINAL TECHNICAL 8/15/87 - 2/14/91

4. TITLE AND SUBTITLE	5. FUNDING NUMBERS
DESIGN OF POLYMERS WITH SEMICONDUCTOR, NLO AND STRUCTURAL PROPERTIES	CONTRACT NO. F49620-87-C-0100

6. AUTHOR(S)

PROFESSOR LARRY R. DALTON

633240 1693/00

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)	8. PERFORMING ORGANIZATION REPORT NUMBER
UNIVERSITY OF SOUTHERN CALIFORNIA CHEMISTRY DEPARTMENT, SEELEY G. MUDD RM. 418 LA CA 90089-1062	AFOSR-TR- 91 0497

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)	10. SPONSORING/MONITORING AGENCY REPORT NUMBER
DEPARTMENT OF THE AIR FORCE AIR FORCE OFFICE OF SCIENTIFIC RESEARCH (AFSC) BOLLING AIR FORCE BASE, DC 20332 - 6448	F49620-87-C-0100

11. SUPPLEMENTARY NOTES

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12a. DISTRIBUTION/AVAILABILITY STATEMENT	12b. DISTRIBUTION CODE
APPROVED FOR PUBLIC RELEASE: DISTRIBUTION UNLIMITED	

13. ABSTRACT (Maximum 200 words)

NOVEL MONOMERIC AND POLYMERIC MATERIALS WERE DESIGNED, SYNTHESIZED AND INVESTIGATED FOR NONLINEAR OPTICAL ACTIVITY. RIGID PROCESSIBILITY REQUIREMENTS LEAD TO APPROPRIATELY FUNCTIONALIZED VERSIONS OF PREVIOUSLY INTRACTABLE DOUBLE STRAND OR "LADDER" POLYMERS, DEMONSTRATING A THIRD ORDER RESPONSE COMPARABLE TO POLYACETYLENE BUT ON A STABLE AND ROBUST LADDER POLYMER FILM. METALLATED ORGANIC COMPLEXES WERE DEVELOPED WHICH SHOWED STRONG NLO RESPONSE IN SOLUTION; THIS ENCOURAGING RESULT WILL BE FURTHER INVESTIGATED. ANILINE/THIOPHENE COPOLYMERS WERE DEVELOPED THROUGH A SOLUBLE PREPOLYMER ROUTE, ALLOWING FOR THE CASTING OF THIN FILMS FROM SOLUTION WHICH ARE THEN THERMALLY ANNEALED RESULTING IN RING CLOSURE AND THE FORMATION OF TOUGH DURABLE FILMS.

14. SUBJECT TERMS		15. NUMBER OF PAGES
ELECTROACTIVE, NONLINEAR OPTICAL, POLYMER, SEMICONDUCTOR (ORGANIC).		46
		16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
UNCLASSIFIED	UNCLASSIFIED	UNCLASSIFIED	

NSN 7540-01-280-5500

Standard Form 298 (Rev. 2-89)

FINAL TECHNICAL REPORT 8/15/87 - 2/14/91

AIR FORCE OFFICE OF SCIENTIFIC RESEARCH

CONTRACT NUMBER F49620-87-C-0100

"DESIGN OF POLYMERS WITH

SEMICONDUCTOR, NLO AND STRUCTURAL

PROPERTIES"

Prepared by Professor Larry R. Dalton, Department of Chemistry, University of Southern California, Los Angeles CA 90089-1062

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Final Technical Report

Introduction

A major objective of this research program has been to explore unique optical effects which we have speculated to exist in ladder polymers. By steadily improving the solubily and processability through utilization of derivitization and precursor routes we have been able to form the first optical quality films of a ladder polymer and have achieved high resolution characterization of optical nonlinearity in these materials. We have thus succeeded in all our stated objectives, in addition we have examined for the first time numerous other systems of promising optical nonlinearity. Details of the sythesis, characterization and optical measurements of the most promising of the systems examined is contained in the body of this report. At the moment it is sufficient to say that an enormous amount of original research has been achieved through direct support of this grant, a measure of this can be readily seen if one examines the accompanying bibliography of manuscripts published through AFOSR support .

In more detail, steady progress has been achieved on our "core" systems of ladder polymers and oligomeric units of ladder polymers introduced as the electroactive units in block copolymers. Utilization of electroactive unit of defined quantum confinement length linked by a non-active aliphatic "spacer" has enabled us to overcome the problems of band edge smearing and lack of processability of more traditional ladder polymers. An example of this research was presented at the July 1990 SPIE meeting in San Diego, CA, reference SPIE proceedings 1990. In addition, a number of new systems of potential as usable $\chi^{(3)}$ materials have captured our attention and are currently under examination, including squaric acid and squarillium derivatives and nickel metallated tetraazo-annulene complexes. Most excitingly, progress has been achieved in the examination of mixed-valence complexes, which have potential applications as second or third order materials. Preliminary measurements on dilute aqueous solutions of the mixed $Fe(II)/Fe(III)$ cyanide complex prussian blue have revealed a large NLO response - because of the high dilution factor this is seen as a promising result and we are presently investigating more concentrated (i.e., film) forms. We are also investigating synthetic routes to more processable polymeric mixed valence/mixed metal systems involving the use of ionomeric matrices. Progress has also been accomplished in the field of

materials exhibiting second harmonic nonlinear effects. Steady improvements, particularly in the asymmetrically substituted three and five -ring systems, are allowing us to approach device usable numbers. In particular, extension of the conjugated π-electron ring system from three to five units is presently underway, and initial ultraviolet-visible spectrophotometry demonstrates, in line with theory, a red shift towards the near-infrared of approximately 100nm. This corresponds to a narrowing of the bandgap between ground and excited state which is expected to be reflected in an increase in β, the second order microscopic nonlinear-optical susceptibility. Measurements are currently underway to verify this experimentally. As an addition to the work in asymmetrically substituted heterocyclic compounds, the design and synthesis of the more traditional azo-linked compounds, albeit with novel donor/acceptor substitution, is being vigorously pursued. The methodology for incorporation of azo-type dyes into cross-linkable (on exposure to ultraviolet light) polyester polymers has been developed as a means of minimizing relaxation of the chromophore with time, a major problem in any usable device. This subject, and the others mentioned above, will be expanded on in the body of the text. We have also vigorously pursued oxidative and protonic doping studies particularly but not exclusively on our polyene containing systems. We have demonstrated complete bleaching of the $\pi-\pi^*$ bands in the visible region with concurrent appearance of new mid-gap bands in the long visible/NIR region. The accompanying formation of polarons and bipolarons is an exciting phenomenon and their effects as charge carriers in the NLO response is under investigation. For further, in-depth information, please peruse the following bibliography of papers published through the direct support of AFOSR grant F49620-87-C-0100 for references to any pertinent manuscripts.

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Squaric Acid and Squarillium Derivatives

Squaric acid (3, 4-dihydroxy-3-cyclobutene-1, 2-dione) crystallizes in the monoclinic space group $P2_1/m$, and therefore possesses inversion symmetry (i.e., $P2_1/m$ is centrosymmetric).[1] However, surprisingly, crystals of squaric acid give a relatively strong temperature dependent second harmonic generation signal, increasing linearly with temperature to about 340K then falling off rapidly as a result of a non-destructive phase change to body centered tetragonal, space group $I4/m$, symmetry.[2] A possible explanation for this interesting phenomenon is thermally activated motion of the protons to out of plane positions resulting in a dynamic distortion of the inversion symmetry. The nature of the proton movement is from an asymmetric O--H-O bond to a symmetric O--H--O bond as the temperature approaches 370K (this is responsible for the phase change at that temperature). Interestingly, there is no literature report of a third harmonic generation measurement; therefore we have grown large transparent crystals of squaric acid, of prismatic form, by slow evaporation from aqueous solution and intend to examine the magnitude and the temperature dependence of the $\chi^{(3)}$ signal. The transparent nature of the crystal will allow for the use of very high intensity incident beam powers with no optical loss due to lack of absorption at 532nm. It is entirely possible, due to the small mass of the proton, that fast H atom movement can be accomplished under the influence of an intense optical field; it is hoped that such an effect will be accompanied by a large $\chi^{(3)}$ signal.

Derivatives of squaric acid are also being designed, synthesized and examined for the magnitude of any NLO effects. Reaction Scheme one shows the structure of squaric acid and details the synthesis of a three-ring monomer containing the squaric acid moiety. As also shown in Scheme 1, this monomeric squarillium derivative can be polymerized with a variety of acid chlorides to form a series of block copolymers - at the moment the monomer is in hand, and has been characterized by UV-Vis, FT-IR, ^{1}H NMR and elemental analysis. Synthesis of the polymers, by condensation with acid chlorides, is an ongoing area of research. However, careful choice of the acid chloride should provide us with a soluble film forming polymer; meanwhile, the monomer, in the form of a doped composite film, is awaiting examination by the degenerate four wave mixing technique (DFWM) to measure the strength of the time resolved $\chi^{(3)}$ signal.

Reaction Scheme 1: Squaric acid and its derivative monomer and block copolymer
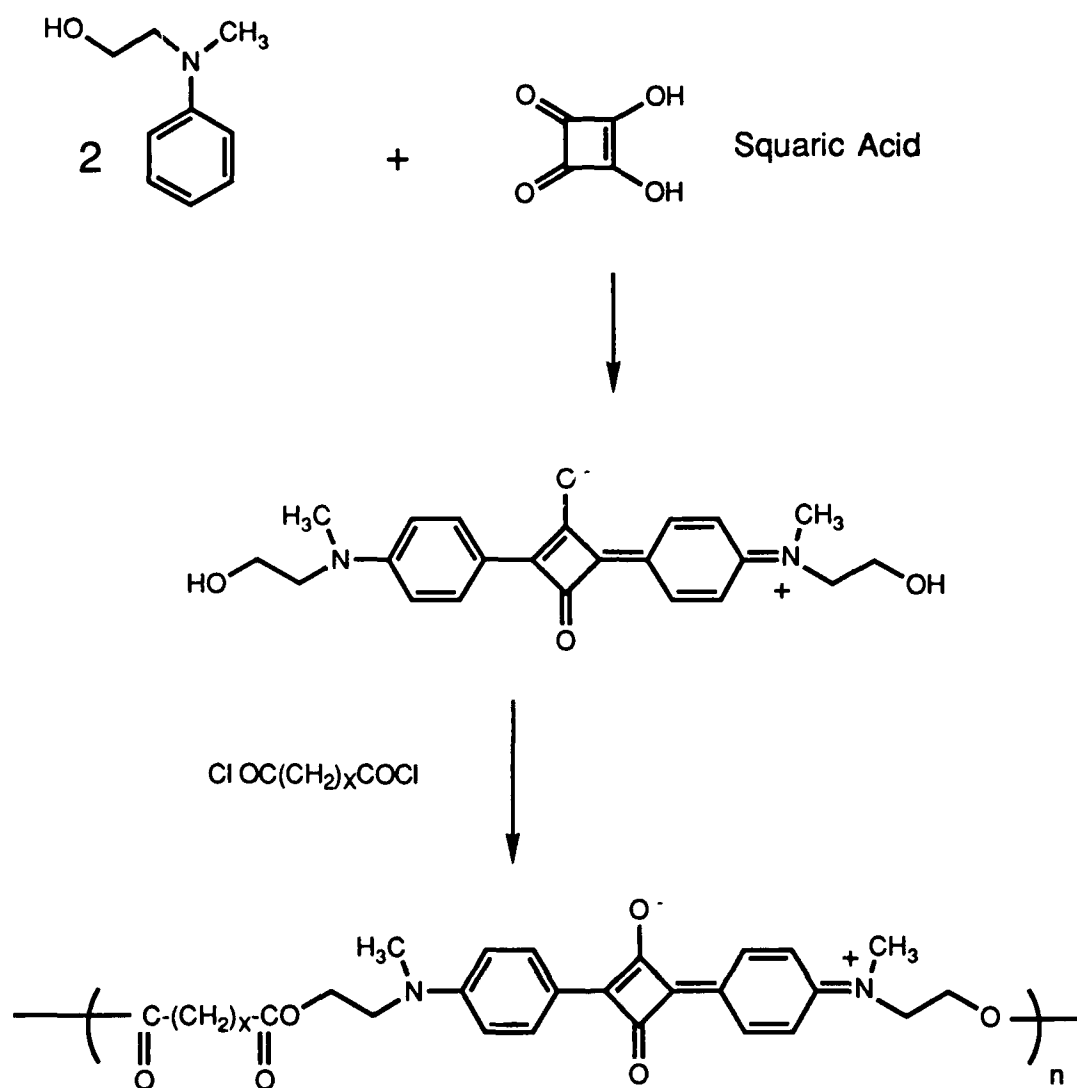

Tetraazaannulene Monomers and Polymers

The extended delocalized π-electron phthalocyanine (Pc) ring systems have demonstrated some of the highest $\chi^{(3)}$ values to date. However, they suffer from a lack of processibility, largely due to their inherent lack of solubility in common organic solvents. To circumvent this problem, we have concentrated on the similar, but less rigidly planar, tetraazannulene (TAN) ring system. Like phthalocyanine, TAN possesses a circular pathway of extended π-electron conjugation, and also contains an inner ring of four nitrogen atoms, capable of ligating a variety of metals in the [2+] valence state. Unlike Pc, TAN contains only two aromatic rings, linked by an ethylene spacer, and therefore

possesses a great degree of solubility in organic solvents, necessary for the fabrication of optical quality thin films. The following Reaction Schemes (2 - 5) demonstrate the synthesis of a TAN containing polymer, by first demetallating nickel TAN (Scheme 2), then synthesizing the flexible spacer unit (Scheme 3), then reacting monomer and spacer together to form a flexible block copolymer (Scheme 4). The R group can be modified to maximize solubility and film forming properties; in this case both R = $(CH_2)_5$ and R = $(CH_2)_{10}$ are being investigated.
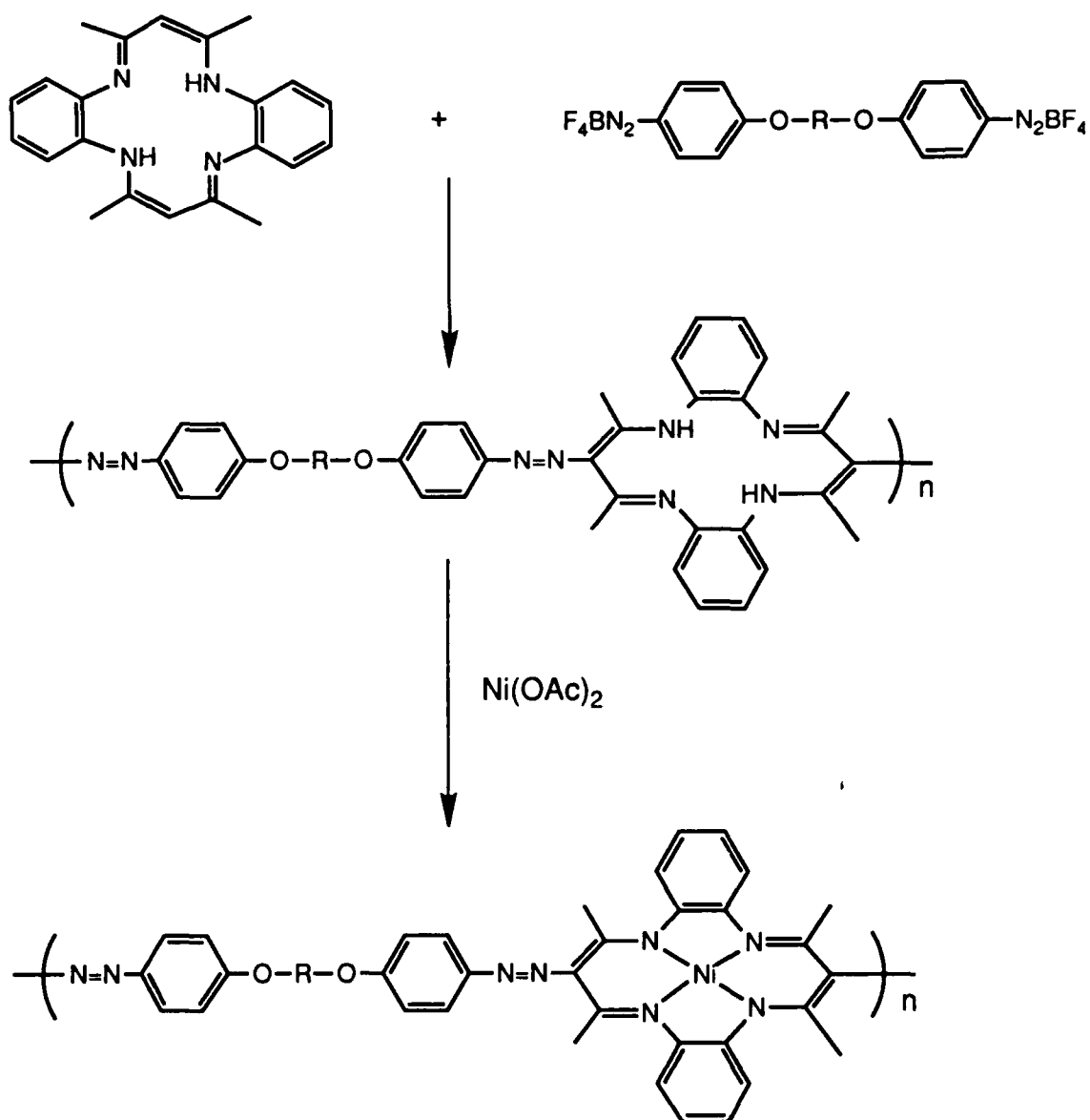
Reaction Scheme 2: Acid induced demetallation of Nickel Tetrazaannulene
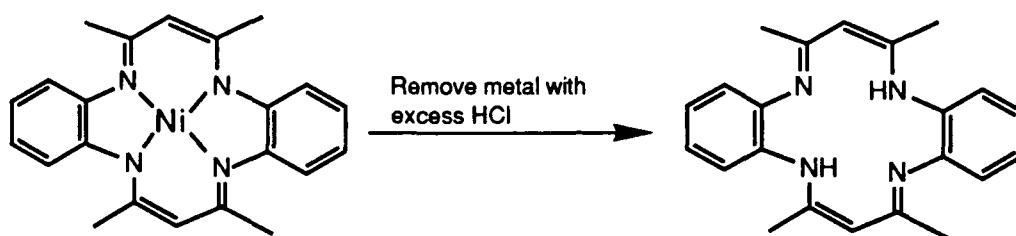
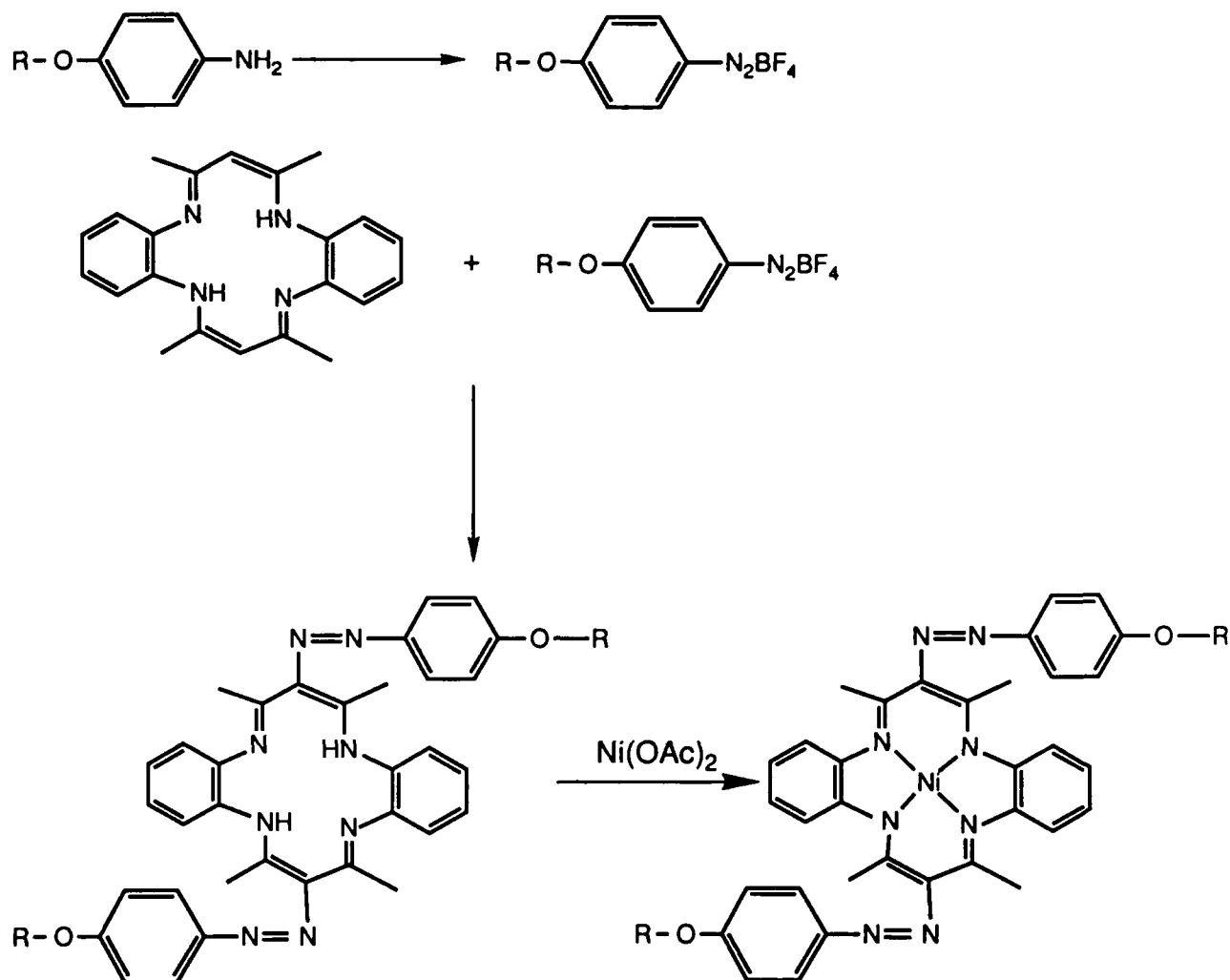Reaction Scheme 3: Synthesis of the flexible "spacer" moiety
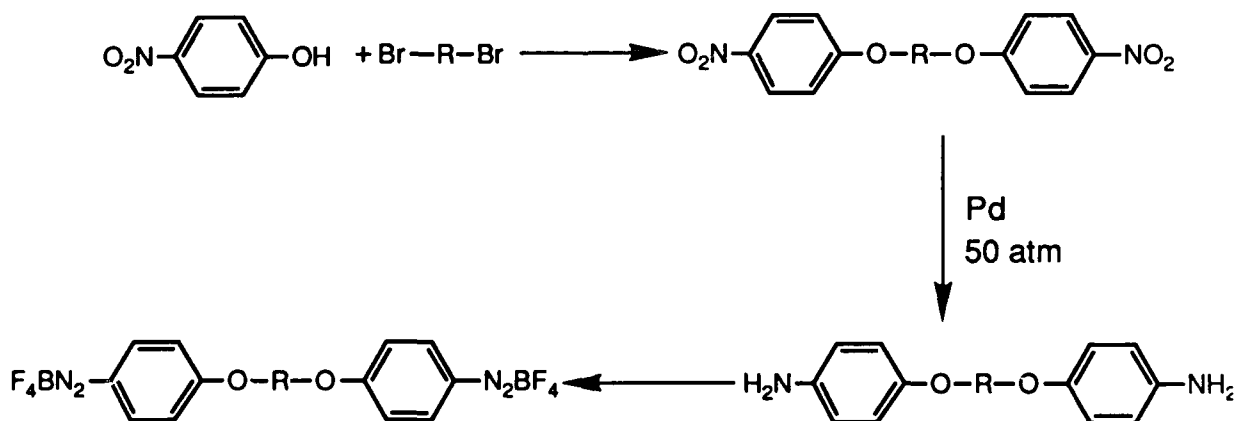
Reaction Scheme 4: Synthesis of the TAN containing block copolymers

R= (CH$_2$)$_5$,   (CH$_2$)$_{10}$

Reaction Scheme 5: Synthesis of a Representative Model Compound

The polymers are green in color and exhibit an absorption maximum at approximately 410nm [metallated with Ni^{2+} and where R = $(CH_2)_5$]. The absorption spectrum shows a minimum at approx. 520 to 540nm, tnerefore there should be minimum absorption and minimum resonance enhancement when the NLO response is measured at 532nm. . The preparation of dust free films of high optical quality is currently underway.

Stabilization of the Second Order Nonlinear Optical Electrooptic Effect by Ultraviolet Initiated Crosslinking of a Doped Polyester

Polyesters containing disperse red dye have been synthesized. These polymers are soluble in many organic solvents and can be processed into thin films by spin-coating. It was found that they exhibit large and stable second order electrooptic effects characterized by second harmonic generation. With

the corona poling method, large resonance enhanced second order nonlinear coefficients, $\chi^{(2)}$, of 590 pm/v for polymer 1 and 280 pm/v for polymer 2 were observed at 532 nm. When these values are extrapolated to 800 nm, the transparent region for these polymers, $\chi^{(2)}$ values of 112 pm/v and 84 pm/v were obtained for polymers 1 and 2, respectively. It has been demonstrated that these $\chi^{(2)}$ values are stable at ca 80% of their maximum values for more than 1000 hr.

Second order nonlinear optical (NLO) polymers have attracted considerable interests in both the industrial and academic communities due to their potential applications in electrooptic devices.[3-14] Three forms of second order NLO polymeric materials have been studied: 1). transparent polymers (including liquid crystal polymers) doped with NLO molecules, i.e. host/guest composite materials;[3-5,12,15,16] 2). Polymers covalently functionalized with second order NLO chromophores[3-5, 7, 9-11, 13,14] and 3). polymers with covalently attached NLO chromophores and then cross-linked after electrical poling.[8] Host/guest polymer composites suffer from limited miscibility of the NLO molecules in host polymers and from the dipole orientation loss due to thermal relaxation. The second type of polymers exhibits much improved stability of NLO activity and a higher density of NLO moieties.[7] The third type of polymer exhibits even greater stability of the NLO activity compared to the first two types. M. Eich et al[8] found that in their cross-linked polymers, there was no detectable decay in second harmonic generation for over 500 hr under ambient conditions and no relaxation tendency even at 85°C. Therefore, cross-linkable polymers are promising materials for NLO applications.

Recently we attempted to synthesize some new NLO polymers in which there exist known NLO moieties with large optical nonlinearities and a cross-linkable unit. Reaction Scheme 6 shows the examples, in which phenylenediacryl chloride monomer is photocross-linkable[17] and diacetylene unit is photo- or thermally cross-linkable.[18] The advantage of this scheme is that many difunctionalized NLO moieties can be incorporated into polymers. In contrast to our expectations, experiments showed that the chromophore bleached when it was exposed to UV curing light, resulting in a dramatically reduced $\chi^{(2)}$ value . The results suggest, on the one hand, that photo cross-linking results in too much trade-off in second order NLO activity; on the other hand, the large change in the refractive index of polymers accompanying photobleaching can be utilized in device fabrication using available photolithographic methods.

Reaction Scheme 6. Synthesis of polymers 1 and 2
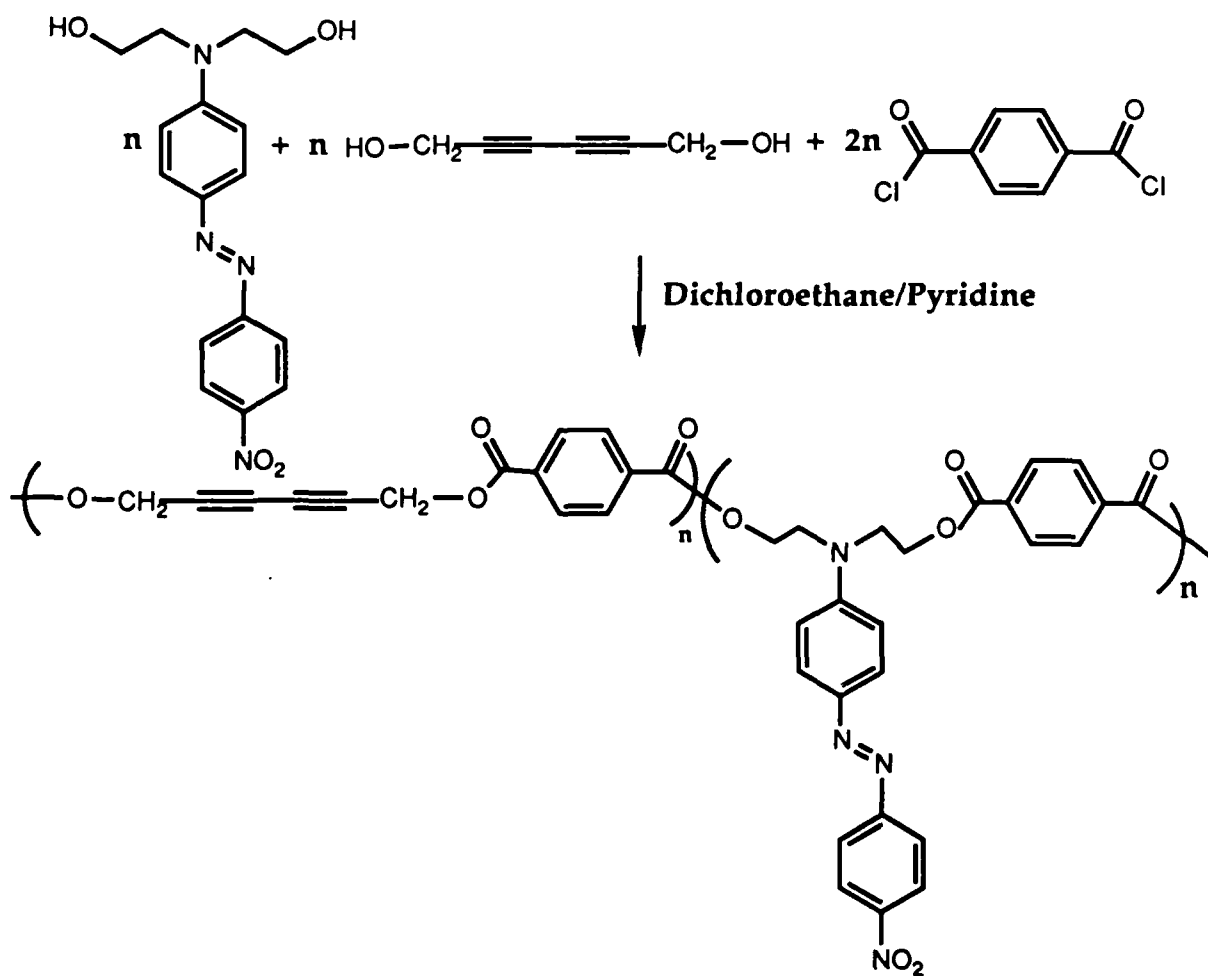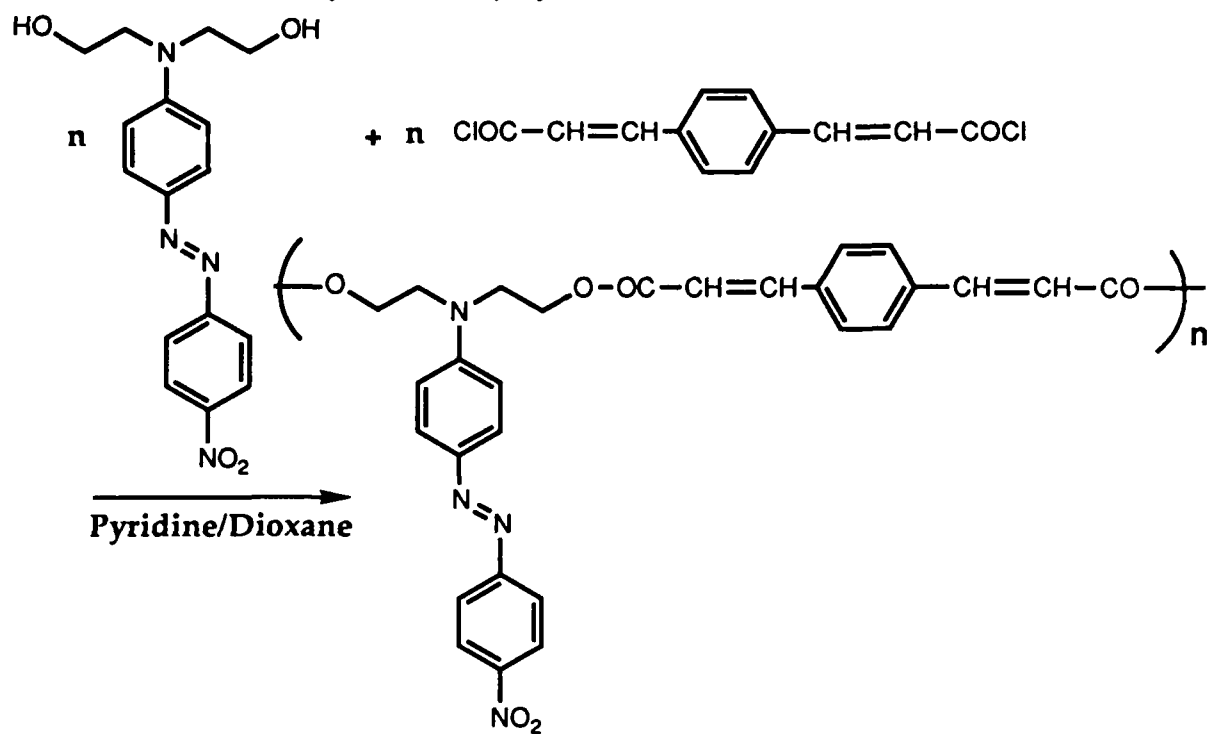
Unexpected , it was found that the polymers without exposure to UV light demonstrated very large $\chi^{(2)}$ values, 590 pm/v and 280pm/v for polymers 1 and 2, respectively.

The polymers outlined in Reaction Scheme 6 were synthesized as follows; Polymer 1. p-Phenylenediacrylic acid (0.5 g, 1.96 mmol) and 2,2'{[4-(4-nitrophenyl)azo]phenyl}iminobisethanol (disperse red 19) (0.647 g, 1.96 mmol) were dissolved in dioxane (15mL) and pyridine (0.5 mL) was added to the solution. The mixture was heated to reflux for 2 hr under Argon atmosphere. The resulting polymer solution was poured into ethanol (20 mL) and the polymer precipitate was collected by filtration and washed with ethanol. The polymer was further purified by extraction in soxhlet extractor with ethanol and dried under vacuum overnight, yielding polymer 1 (0.94g, 94%).

Polymer 2. To a three-necked flask were added 1,6-dihydroxy-2,4-hexidiyne[19] (0.524 g, 4.75 mmol), disperse red 19 (1.569 g, 4.75 mmol), dichloroethane (10.0 mL) and pyridine (3.0 mL) and then terephthaloyl chloride (1.93 g, 9.50 mmol) dissolved in dichloroethane (10 mL) was added dropwise to the mixture. The resulting mixture was heated to 70°C for 2 hr. and was then poured into ethanol. The polymer precipitate was collected and handled as for polymer 1, (3.32 g, 90%).

The second harmonic measurements were performed in the setup shown in Figure 1. A Spectra-Physics Nd:YAG laser was used as a fundamental source. The polymers were dissolved in solvent and filtered, then spin-cast on transparent glass substrates with an ITO conductive layer as the poling electrode. The polymer film thickness ranged from several hundred to several thousand angstroms. The dried film was then heated to near or above its glass transition temperature T_g and corona poled with an intense dc electrical field, as shown in Figure 2. The polymer film was cooled down to room temperature in the presence of an electrical field.

Figure 1. Schematic diagrams of second harmonic generation experimental setup. P-polarizer, BS-beam splitter, S-sample polymer film, F-fundamental wavelength filter, ND-neutral density filter, D1,D2-detectors, OSC-oscilloscope, Boxcar-boxcar integrator.
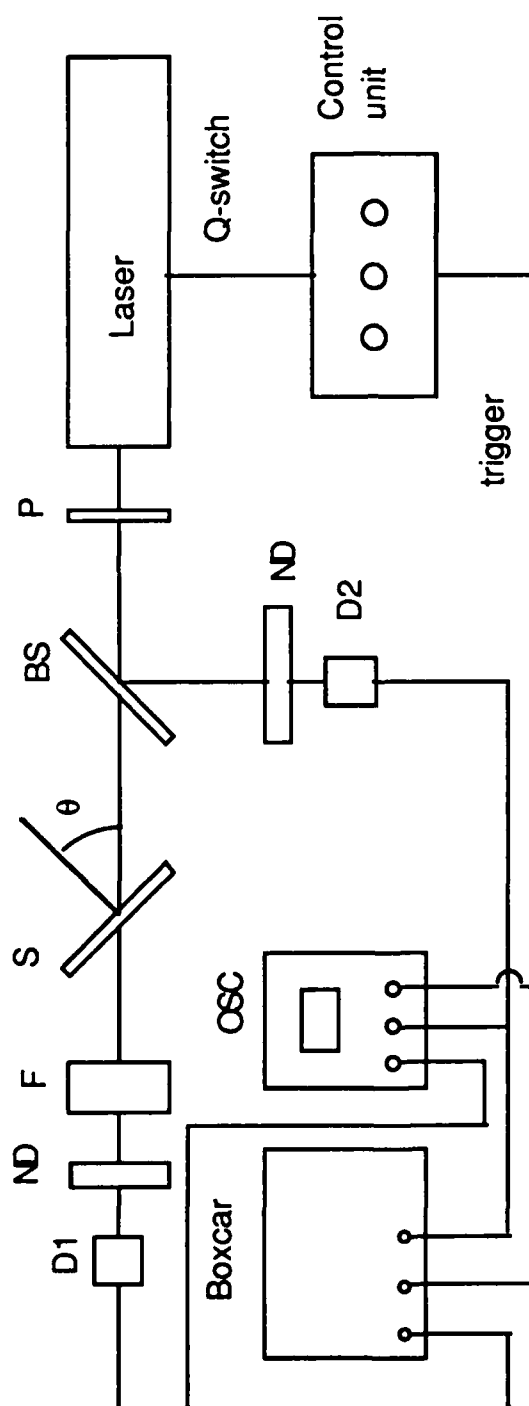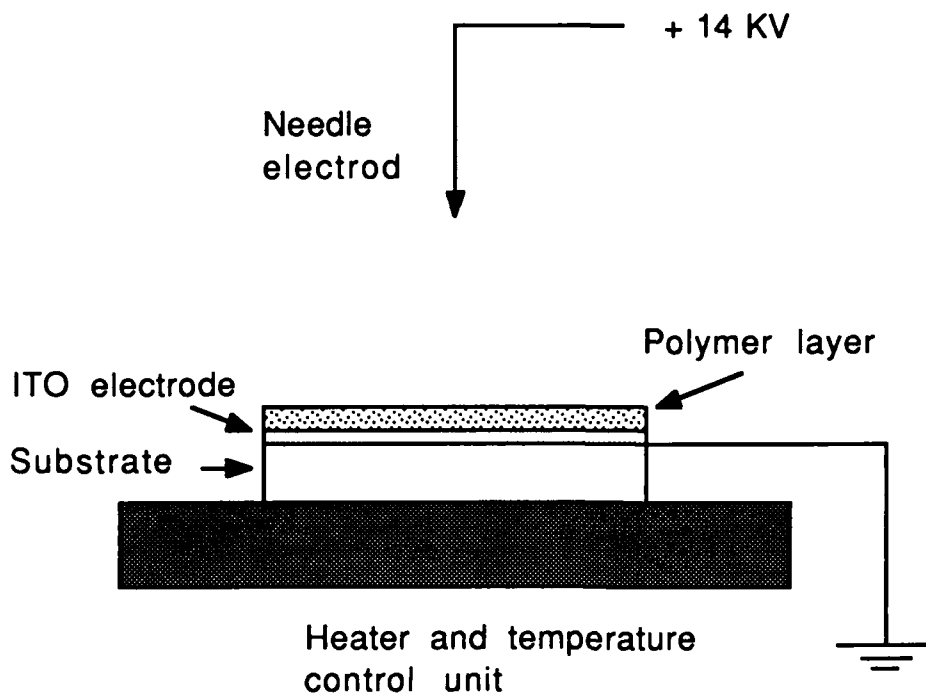
Figure. 2. Corona poling apparatus used in poling polymer thin films.

The second harmonic coefficients of the polymer films were calculated by comparing their second harmonic intensity with that generated by a quartz standard[19].

Since disperse red dyes have shown large second order NLO effects,[20] we utilized the difunctionality of disperse red 19 to prepare linear polymers. The initial aim of this work was to synthesize cross-linkable second order NLO polymers. As mentioned above, the cinnamic group is a well-known photocross-linkable unit[17] and diacetylene can be cross-linked through thermal or light treatments;[18] therefore we chose phenylenediacryl chloride as monomer in the synthesis of polymer 1 and incorporated the diacetylene unit into polymer 2. Both polymerizations were carried out in dioxane or dichloroethane and the resulting polymers were identical. The polymers obtained are partially soluble in chloroform, THF, DMSO, DMF and soluble in m-Cresol and NMP. Optical quality films can be cast using the spin-coating technique. GPC measurements show that the weight averaged molecular weights are 4800 and 5000 for polymers 1 and 2, respectively, using polystyrene as standard. Elemental analysis results fit the polymer structure drawn in Scheme 6.

^{1}H NMR spectra of polymers 1 and 2 are consistent with the structures shown in Scheme 6. For polymers 1 and 2, the chemical shifts of methylene group in disperse red 19 unit appear at 3.8 and 4.5 ppm, respectively. The chemical shift due to vinyl proton of polymer 1 appears at 6.3 ppm with multiple peaks which could be due to an end-group effect. The spectrum of polymer 2 shows a -O-CH$_2$-C=C- chemical shift at 5.0 ppm. It has the same integration area as those for either -OCH$_2$- or -NCH$_2$- and is a further support for the polymer composition drawn in Scheme 6.

FTIR spectra of polymers 1 and 2 show absorptions due to nitro groups around 1520 and 1350 cm^{-1}. For polymer 2, the carbonyl absorption appears at 1730 cm^{-1} while the carbonyl absorption in polymer 1 appears at 1720 cm^{-1} due to conjugation with vinyl group. The absorption band due to vinyl group in polymer 1 is around 990 cm^{-1} and the absorption due to the diacetylene unit in polymer 2 appears around 2200-1950 cm^{-1}.

The thermal properties of these polymers have been studied employing DSC and TGA. DSC traces for both polymers give Tg values of 120 and 122 °C for polymers 1 and 2, respectively. For polymer 1, a melting transition occurs at 183°C which has been supported by melting process observation and TGA data; when the polymer was heated in a melting tube, the molten state has been observed at around 190°C and the TGA trace of polymer 1 shows no weight loss until 250°C. For polymer 2, the process at 200°C is a much broader, exothermic process and might involve more complicated process. TGA data show slight weight loss starting at 200°C and a fast decomposition at 250°C.

UV/vis spectra of the polymers, measured in thin films, show absorptions in the visible region around 470 and 455 nm . These polymers have been tested for photoinduced cross-linking using a mercury lamp as UV light source. When the polymer thin films are exposed to UV light, photobleaching was observed. The relationship between refractive index and exposure time was explored for polymer 6. It was seen that as exposure time increases, the refractive index decreases. After 40 minutes of exposure, the refractive index then retains a stable value. Solubility change has been observed for UV light exposed polymer thin films; the spot exposed cannot be washed out with chloroform while the area unexposed can redissolved in chloroform. Furthermore, second harmonic generation measurements show a considerable decrease in second order NLO coefficients for both polymers after exposure. These refractive index changes and decreases in second order NLO coefficients could be due to photoinduced cis-trans isomerization of the azo-unit

in NLO chromophores and/or some photochemical processes. But after thermal annealing at 200°C or light illumination using a 250 nm UV source, we cannot recover the reduced refractive index as with other azo dyes, which suggests that either the cross-linked polymer matrix hinders cis-trans isomerization or some permanent photochemical reaction destroys the NLO chromophore. FTIR spectra detected a decrease in the intensity of vinyl proton absorption in polymer 1 before and after exposure, but the change is too small to permit meaningful conclusions to be drawn. Further studies are in progress.

Although photobleaching reduces the NLO effect, the large index change of these polymers makes it possible to use available photolithographic methods in device fabrication. Detailed results will be reported elsewhere.[22]

The second order optical nonlinearity has been characterized via second harmonic generation (SHG). From measured second harmonic output, thin film refractive indexes, thickness and absorbance at second harmonic wavelength, we obtained d_{33} values of 295 pm/v and 140 pm/v for polymers 1 and 2 at 1064 nm fundamental wavelength. These d_{33} values can be converted to $\chi^{(2)}$ values , thus, $\chi^{(2)}$ values of 590 pm/v and 280 pm/v for polymers 1 and 2 were obtained. The difference of $\chi^{(2)}$ values for these two polymers mainly comes from the difference in chromophore density. If we take $C_{16}H_{16}N_4O_4$ as formula of chromophore, the weight percentage of chromophore in polymers 1 and 2 are 68% and 47%, respectively. Obviously these measured d_{33} values were resonance enhanced since the absorption peaks, which were at 470 nm for polymer 1 and 455 nm for polymer 2, were not far away from the second harmonic wavelength. For integrated optic applications, semiconductor lasers are the major light sources and transparent electro-optic materials are usually used. Hence, the second order NLO coefficients near infrared wavelength are more important. Using a simple two level model, the measured $\chi^{(2)}$ values were extrapolated to 800 nm (near infrared) wavelength where the polymer films are transparent and thus obtained d_{33} of 56 pm/v for polymer 1 and 42 pm/v for polymer 2. The corresponding electro-optic coefficient r_{33} calculated were 26 pm/v and 24 pm/v, respectively. These polymer materials showed a high stability in second order NLO effect. The temporal behavior of second harmonic coefficients of polymer 1 and 2 was examined. It was seen that the second harmonic coefficients, $d_{33}(t)$, were stabilized at 80-90% of their maximum values, $d_{33}(0)$, after more than 1,000 hours . Comparing these polymers with those doped with NLO molecules and those covalently functionalized with NLO moieties,[7,8] we can note that the $\chi^{(2)}$ values of these polymers are among the largest , stable second order

coefficients reported. The NLO properties are promising in practical applications, such as the fabrication of a waveguide. Primary study shows that reasonable waveguiding has been achieved based on these materials.

Electroactive Properties of Diphenylpolyenes and Diphenylphenylenevinylenes

Our research group, in collaboration with Spangler and coworkers (University of Northern Illinois), have accomplished the full characterization of the electroactive properties of diphenylpolyenes and diphenylphenylene-vinylenes . These characterizations cover a broad range from optical and electron spin resonance (ESR) studies of pristine and oxidatively doped compounds to conductivity and non linear optical (NLO) measurements.

The formation of polaronic and bipolaronic species have been confirmed by both optical spectroscopy and ESR. It was reported by Spangler and coworkers that p,p'-disubstituted diphenylpolyenes could be doped with excess antimony pentachloride ($SbCl_5$) in solution, with complete optical bleaching of the original π to π^* transition and the appearance of new bands at lower energies in the visible and near IR regions.[23] Delocalization stabilization was improved with the transition energies of the midgap species decreasing as n was increased from 3 to 6, and as the electron donating ability of the para-substituent was increased (H < Me < MeO < Me_2N).[24] It was established that bipolarons were more stable in solution than polarons by noting the decay of ESR signals.[25] They have also shown that polaronic and bipolaronic formation can be controlled selectively with varying concentrations of dopant.[26]

Recently, our research group accomplished the solid state doping of these compounds with iodine and reported the conductivity measurements on pressed pellets.[27] The effects of conjugation length and substituents on the conductivity were found not to correlate with the previously reported optical studies of the solution doped compounds. This is expected in light of the fact that optical measurements are microscopic measurements of the system, whereas conductivity measurements are macroscopic measurements of the system.

The highest conductivity was observed for the p,p'-dimethylamino-hexatriene (see Table I) and ESR studies correspond well with the reported conductivities, where asymmetrical narrow signals were displayed for high values and symmetrical broad signals were displayed for lower values. The ESR signals of the dimethylamino substituted compounds exhibit the effects of g-anisotropy which is clearly seen in the ability to distinguish between the $g_\perp$

and $g_{\parallel}$ contributions. It was expected that upon the formation of polarons via doping, that the g-anisotropy would become averaged. Indeed this is what was observed for the doped samples; the signals were an order of magnitude larger in intensity than those of the undoped materials, which indicated significant amounts of polaron formation upon doping. The signal was also narrower as a result of the averaging of the g-anisotropy which corresponded to electron movement .

Table I MEASURED CONDUCTIVITY

Substituent	n	S $(\Omega^{-1}$ cm$^{-1})$	Substituent	n	S $(\Omega^{-1}$ cm$^{-1})$
Me$_2$N	6	1×10^{-3}	MeO	6	1×10^{-4}
	5	2×10^{-3}		5	6×10^{-4}
	4	1×10^{-4}		4	9×10^{-3}
	3	5×10^{-2}		3	2×10^{-6}

These studies indicate there were no significant effects on measured conductivities for p,p'-disubstituted diphenylpolyenes with varying substituents and/or conjugation length. It appears that the major factor contributing to conductivity was the packing and the intermolecular interactions between the molecules in the solid state. Although preliminary investigation into the packing and solid state nature of selected polyenes has been accomplished by Spangler and coworkers, a complete picture of the solid state nature of the studied compounds has not been achieved at this time.[28]

From these studies we can make a prediction about NLO properties of the diphenylpolyenes. It is interesting to note that even on the timescale of the ESR experiment (nanoseconds), that the electrons do not move fast enough in the doped materials to average out all g-anisotropy. Hence, it can be predicted that the formation of midgap species will not contribute to the non-linearity of these materials, because the timescale of an NLO experiment is even shorter (femto-picoseconds), and the movement of the electrons would be too slow to make any contribution to the delocalization. Measurements of the third order susceptibilities of the undoped and doped materials are in progress.

We have succeeded in preparing composite films of the dimethylamino substituted diphenylpolyenes with polyvinyl alcohol (PVA). The films were cast from trifluoroacetic acid (TFA), and correspondingly protonically doped to exhibit the same formation of midgap species observed in solution doping with

SbCl$_5$ and solid state doping with iodine. Unfortunately, as of this time, we have not been able to incorporate significant concentrations of the polyenes into the PVA matrices to obtain third order NLO measurements. The symmetrical character of the diphenylpolyenes limits the solubility in most common organic solvents, therefore, we have chosen an alternative route to investigating the NLO properties of these materials.

We recently reported the incorporation of diphenylpolyene , phenylene-vinylene, and thiophenevinylene segments into copolymeric systems (see Figure 3).[29] This not only allows us to increase the concentration of the electroactive unit, it also allows us to investigate the effects of conjugation length of the segments on the NLO measurements.

We have achieved optical quality films of these copolymers from TFA, and NLO measurements have been accomplished (Figure 4). As can be noted, the copolymers need to be incorporated at a concentration of at least 10 percent (relative to dodecanedioic acid). Also of interest is the appearance of photochemical degradation in the polyenes. Although this excludes these materials from device applications, we are convinced that fundamental relationships between chain length and the magnitude of the initial NLO response will be achieved as we continue to fabricate copolymers with longer chain lengths. We are also interested in formation of other polyene incorporated copolymeric systems (i.e., polyesters), and investigations of their NLO properties.

27

$X = 0.05$ to 0.27

$x = 6, y = 12$
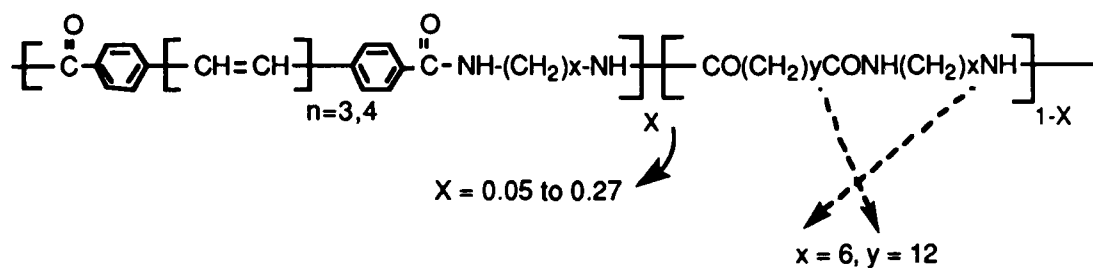
Polymer	% Incorp.	Polymer	% Incorp.
$[C=C]_{n=3}$	5	$[C=C]_{n=3}$	50
$[C=C]_{n=3}$	10	$[C=C]_{n=4}$	10
$[C=C]_{n=3}$	20	$[\bigcirc\!\!-C=C]_{n=2}$	10
$[C=C]_{n=3}$	27	$[S\!\!-C=C]_{n=2}$	10

Figure 3. Copolymers Incorporating Polyene Units

Polymer	% Incorp.	χ^3/α (esu-cm)
$[C=C]_{n=3}$	10	---[a]
$[C=C]_{n=3}$	20	---[a]
$[C=C]_{n=4}$	10	1.4×10^{-13}
$[\bigcirc\!\!-C=C]_{n=2}$	10	---[a]
$[S\!\!-C=C]_{n=2}$	10	0.62×10^{-13}

Figure 4. NLO Measurements for Incorporated Polyene Systems

Aniline Thiophene Copolymers

Copolymers of aniline and thiophene copoly(thiendiyl-1,4-di-aminophenylenes) were prepared by reaction of dibromothiophenes with p-phenylenediamines under Ullmann condensation conditions. Complete characterization including infrared analysis, ultraviolet-visible measurements, detailed thermal measurements, electrical conductivity, ESR and magnetic susceptibility measurements have been performed and reported [30-32].

The reaction temperature had a dramatic effect on the structure of the final product (Scheme 7). Thermal decomposition of the thiophene rings led to a fused polymer (low sulfur) with limited solubility, whereas materials formed at lower temperature retained an unfused structure (high sulfur). The monomers and the polymers synthesized are shown in Figure 5 and Table II below. Although the molecular weights were relatively low, (15-40 thousand amu), the materials displayed excellent thermal resiliency and in some cases were film forming materials.
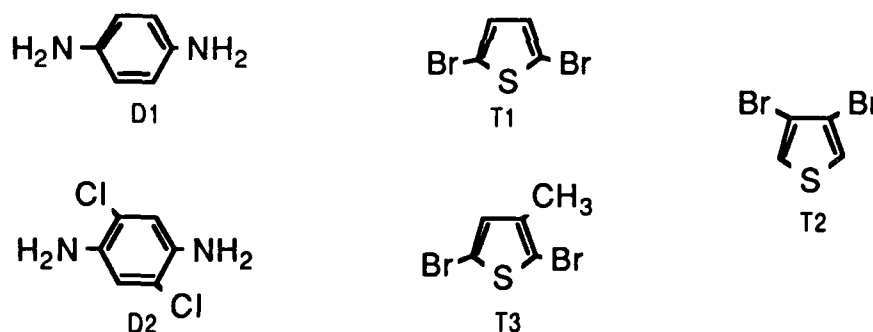
Figure 5. Structure of Monomers

Heat stabilities of up to approximately 500°C for fused materials and up to approximately 250°C for unfused materials were noted. Figure 6 shows thermal gravimetric analysis (TGA) for several of the polymers.

Figure 7 shows the thermal mechanical analysis (TMA) for the copolymers. In unfused materials the coefficient of thermal expansion is approximately four times greater than in fused materials. This result immediately suggests a pattern of expansion. The unfused materials displayed more of a "spaghetti" type nature, while the fused materials appeared more rigid, resisting the tendency to expand and slide over each other.

Table II. Sulfur Content and Identification of Polymers

Polymer ID	D1[a]	D2[a]	T1[a]	T2[a]	T3[a]	Temp. (C)	Sulfur (Exp//Calc)
1	X	—	X	—	—	250	8.06/17.03
1b	X	—	X(0.7)[c]	X(0.3)	—	250	3.06/17.03
2	X	—	—	X	—	250	1.46/17.03
2b	X	—	X(0.3)[c]	X(0.7)	—	250	2.97/17.03
3b	X	—	X	—	—	200	3.91/17.03
4	X	—	X	—	—	200	23.35/17.03
5	X	—	—	X	—	185	24.54/17.03
6	X	—	X	—	—	185	15.99/17.03
7	X	—	—	—	X	185	18.53/15.85
8	—	X	—	—	X	185	13.21/11.82
9	—	X	X	—	—	185	12.66/12.47

a) Monomers shown in Figure 1   b) at 1 atmosphere of nitrogen
c) 0.7, 0.3 refers to molar percentages with respect to diamine
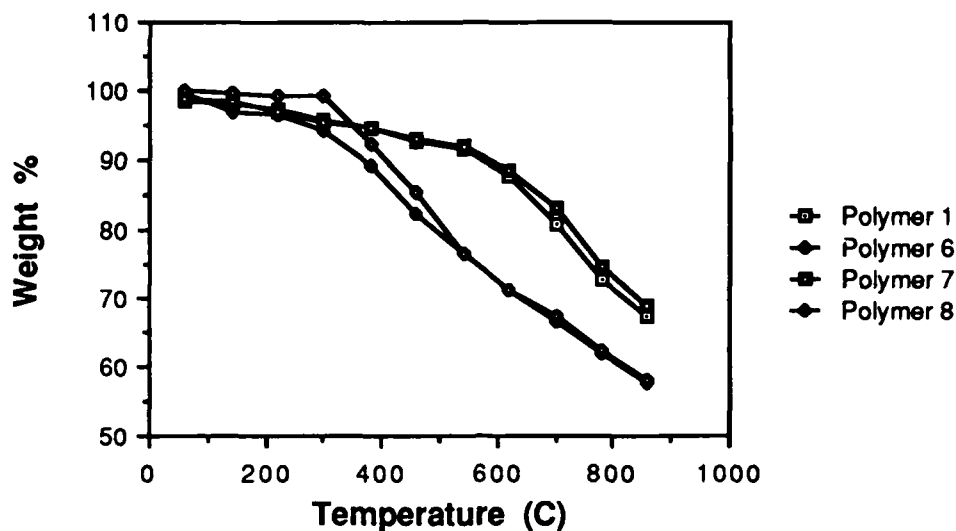
Reaction Scheme 7
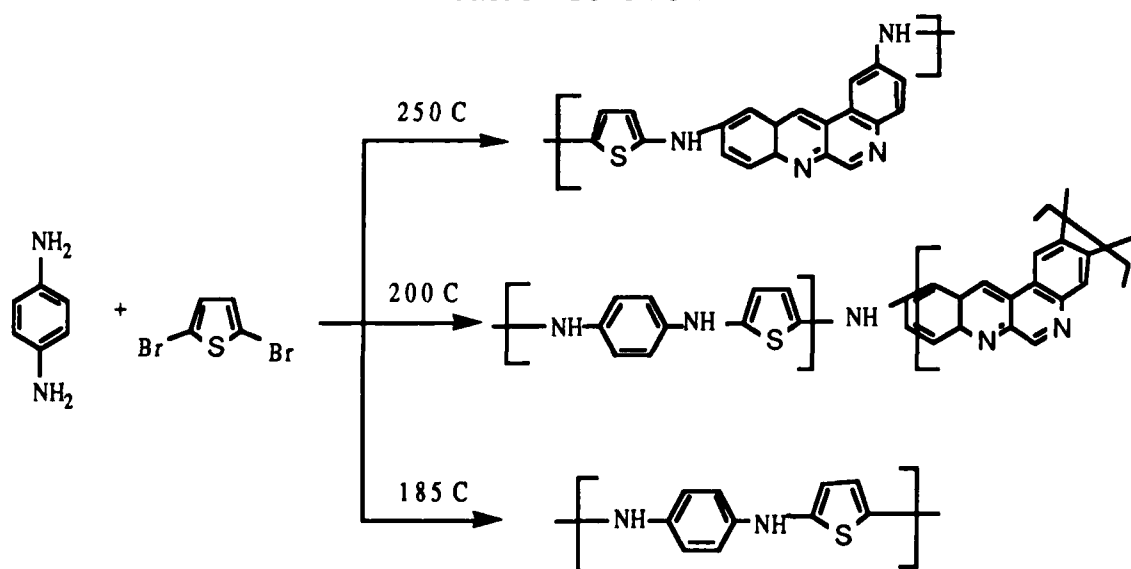
Figure 6. TGA Traces for Fused and Unfused Polymers
(#1 and #7 Fused, #6 and #8 Unfused)
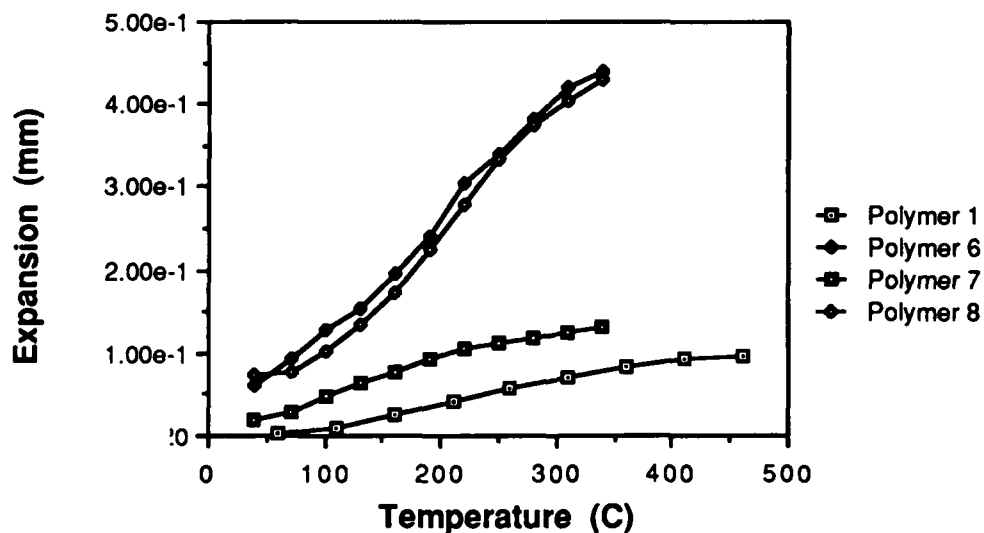
Figure 7. TMA Traces for Fused and Unfused Polymers
(#1 and #7 Fused, #6 and #8 Unfused)

Comparison of the materials produced at higher reaction temperatures (fused) with those formed at lower temperatures (unfused) indicated that the sulfur atom strongly interacts with spin carrying defects, thereby determining the electronic and magnetic character. Magnetic susceptibility measurements on the 2,5-copolymers revealed anomalous temperature independent paramagnetism, or Pauli susceptibilities (X_P), which are usually associated with

metals. At very low temperatures (<50 K), a Curie tailing is present. In the presence of increasing thermal energy , the localized spins which exhibit Curie law behavior (χ 1/T) are randomized and eventually lose influence to a more temperature independent spin character (Figure 8). The materials deficient in sulfur content tend to remain linear following more of a Curie-Weiss relationship where χ 1/(T + Q).
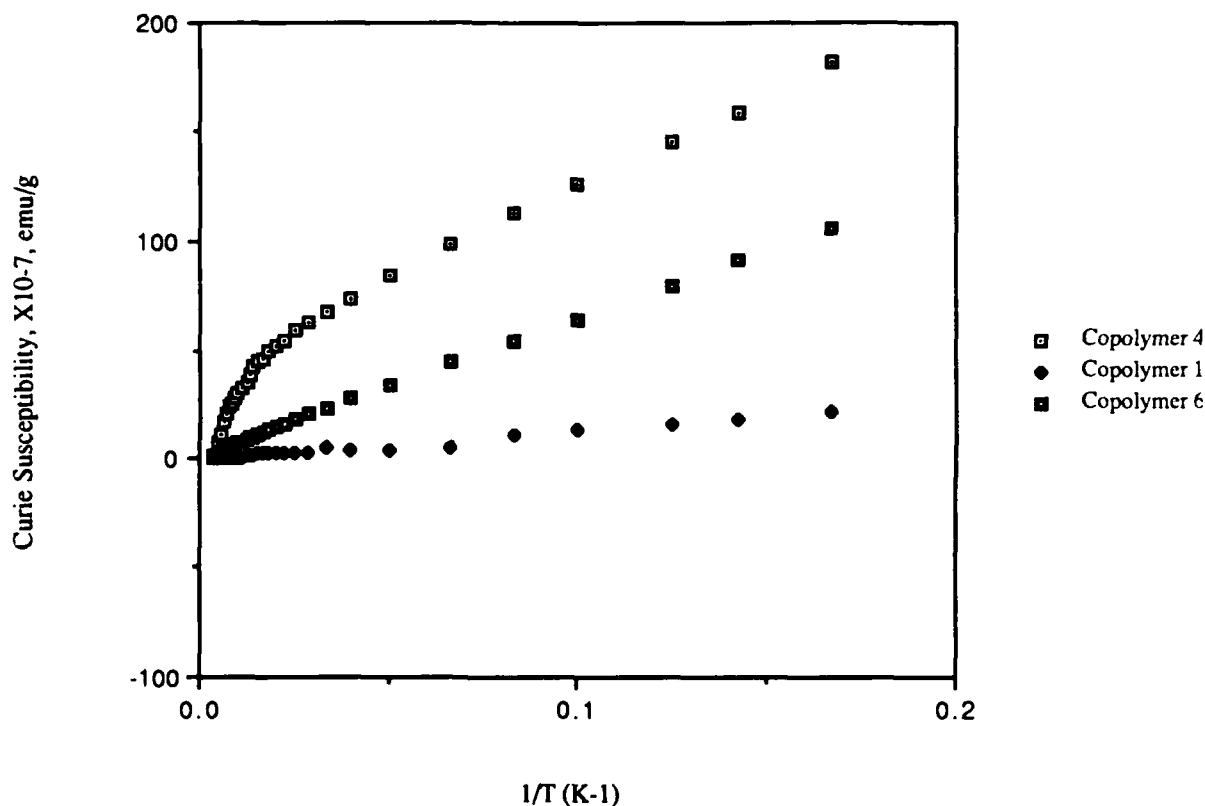
Figure 8. Curie Susceptibilities of 2,5 PTAPS (#1 fused, #4 and #6 unfused)

Certain copolymers exhibited structure in their ESR spectra. Copolymers 1, 4, 6, 8 and 9 all displayed lineshape anomalies. The temperature independence of both the lineshape and linewidth ($\Delta(H_{pp}) \leq 1$ Gauss) indicated that the spins involved in the resonance process are localized, most likely immobilized by the amorphous nature of the material.

All pristine materials behaved as insulators, exhibiting bulk conductivities less than 10^{-12} S/cm. Electron spin resonance studies of the nitrosyl doped materials indicated that these particular dopants reacted with the aniline thiophene copolymers to alter them in an irreversible way. Iodine doped

materials had enhanced conductivities on the order of 10^{-6} S/cm and are listed in Table III.

Table III. Conductivities of Several Aniline Thiophene Copolymers.

Polymer(doped with Iodine)	$S\ (\Omega^{-1}\ cm^{-1})^a$
5)	5.22 X 10^{-6}
6)	2.37 X 10^{-6}
8)	4.64 X 10^{-6}
9)	2.53 X 10^{-6}

a) Measured at 298 K, 1 atm.

Measurements of the third harmonic NLO susceptibilities were performed on selected samples by degenerate four wave mixing experiments. Values of the third order NLO susceptibility of approximately 4 X 10^{-10} esu were obtained along with high laser damage thresholds (4 GW/cm^2), and low absorbances. In addition composite films in poly(vinylalcohol), poly(methylmethacrylate), or poly(carbonate) gave significant χ^3 values in less than 10 percent w/w concentrations (Table IV).

The complete characterization of aniline thiophene copolymers afforded a better understanding of the difficulties of characterization in fused nitrogen containing polymers. Also, insight into the nature of the charge carriers and the influence of the sulfur heteroatom on the magnetic and spin character was realized. Further studies into these systems was halted due to the inherent insolubility of the systems, however, the employment of monomers such as hexadecyl-2,5-diamino phenylether (Figure 9), may produce materials which are much more soluble, and hence, more useful technologically.
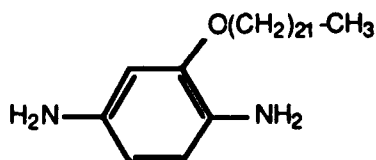

Figure 10. Dodecyl-2,5-diaminophenylether Monomer

Table V. NLO measurements neat film and composite polymer in
Poly(vinylalcohol)

|	25 Fused Neat Film	PVA Composite
Refractive Index	1.67	2.58
Absorption (um-1)	0.93	0.27
C1111 (X10-10 esu)	2.30	1.20
C1221 (X10-10 esu)	1.30	0.40
X t (X10-10 esu)	2.70	0.50

Electrochemical Attachment of Polyaniline to a Copolymeric Support

Throughout the 1980's, researchers have reported many examples of conducting polymer composites. Our research group reported the preparation of polymer supported polyaniline prepared by an electrochemical oxidation of aniline onto a poly(styrene-co-p-aminostyrene) coated electrode, resulting in uniform free standing films.[33] The objective of these reports has been to improve the processibility of the otherwise intractable conducting materials while maintaining attractive electrical properties. Researchers at IBM have recently reported the electrochemical preparation of composite films of polypyrrole in poly(vinylchloride).[34] The resulting composite retained the excellent mechanical properties of PVC and exhibited a reasonable degree of conductivity. Another novel technique involved the adsorption of polypyrrole or polyaniline onto various textile fibers forming uniform coherent films with fair conductivities.[35]

We envisioned using poly(p-aminostyrene) as a functionalized support and electrochemically polymerizing aniline off the pendant NH_2 groups (Scheme III). Although Cao reports the chemical grafting of polyaniline onto poly(p-aminostyrene),[36,37] we believe that better control over side reactions, such as cross-linking of the polyaniline chains, could be achieved electro-

chemically. Such side reactions are often unavoidable in the chemical preparation.

Reaction Scheme 8
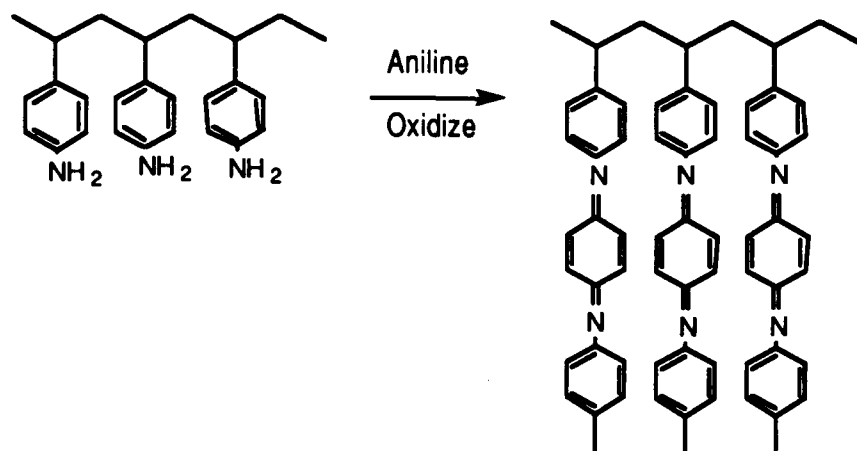
Electrochemical deposition of *polyaniline* onto the support was carried out potentiostatically and by cyclic voltammetry. Several samples were prepared potentiostatically in the range of 0.6 V to 9.0 V. The resulting films exhibited mechanical deformation and ruptured during the electrochemical process. As a result of the deformations it was clear that polymerization was occurring at the surface of the ATO slide and not exclusively on the support. We concluded that potentiostatic methods were not appropriate for production of uniformly incorporated polyaniline composite films.

Uniformly incorporated films were prepared by cycling between -0.2 V to +0.8 V utilizing a scan rate of 50 mV/s on a BAS Model CV-1B cyclic voltammetry apparatus. Cyclic voltammetry was used to compare the polymerization of aniline on the composite film coated electrode and a Pt electrode. At the onset, the copolymer coated electrode had a higher oxidation potential than Pt itself (+0.5 V vs. +0.2 V). After 50 scans the oxidation peak moved from the initial value of +0.5 V to +0.35V (+0.25 V for uncoated ATO). This shift in oxidation potential is easily explained by the conversion of the initial insulating styrene copolymer into a conducting composite, which behaved similar to an electrode.

The uniform green films, obtained by the above process, were washed with deionized water and peeled from the slides. Scanning electron micrographs were obtained which showed the morphology of the polyaniline

particles to be rice-like. This is comparable to the morphology obtained in the preparation of colloidal polyaniline by chemical adsorption processes.[38]

Initial results indicate that polyaniline is indeed chemically attached to the support and not absorbed in the matrix. The resulting films were insoluble in common organic solvents. Infrared analysis shows the appearance of absorption due to the amine salt of polyaniline at approximately 2600 cm^{-1}, the broadening of the aryl NH_2 stretching at 3370 cm^{-1}, and the lowering in intensity of the free C-NH_2 stretching at 1275 cm^{-1}. The electronic (UV-Vis) spectra of the films revealed the appearance of two additional bands after oxidation at 400 nm and 600 nm with a maximum at about 850 nm. This is reasonable in light of the absorption characteristics of polyaniline which span out into the near IR.

Preliminary data on this project has been presented[39]. We plan to expand this method to electrochemical attachment of polypyrrole and polythiophene. The use of this method allows uniform optical quality films, which are difficult if not impossible in the parent conducting polymer.

Synthesis and Characterization of New Polymers Exhibiting Large Optical Nonlinearities. Rigid Rod / Flexible Chain Copolymers.

As part of a continuing exploration of organic and organometallic polymers as nonlinear optical materials, a new copolymer with tripheno-dioxazine rigid rod and aliphatic flexible chain segments has been synthesized. This copolymer exhibits improved processibility and a defined absorption band-edge (with an optical spectrum nearly identical with that of the oligomeric triphenodioxazine model compound) when compared to tradition electroactive polymers which exhibit poor solubility and a diffuse band-edge (partly due to polymer heterogeneity and disorder). Degenerate four wave mixing (DFWM) measurements indicate a third order susceptibility of 4.5 x 10^{-9} esu which demonstrates that no significant sacrifice of optical nonlinearity is required to obtain the desired properties. This study reports a limited investigation of both the temporal response and frequency dependence of the observed optical nonlinearity. By control of reaction conditions, the preparation of several versions of the copolymer is demonstrated, providing insight both into structural electronic property relationships and the role that structure plays in determining solubility.

Incorporation of finite chain length NLO-active units into processible polymers will provide materials with NLO properties similar to those found in extended conjugation polymers. Based on this observation, we have synthesized copolymers with rigid rod and flexible chain segments. We have shown that ladder polymers with quinodioxaline-type units have large third order susceptibilities.[40,41] Triphenodioxazine is a well known dye material[42] which has an extended p-electron delocalization over a five fused ring unit that should be NLO active.[43] We have succeeded in preparing a copolymer with triphenodioxazine and a flexible chain spacer. This polymer has a clearly defined optical band gap, good processibility and high thermal stability. Degenerate four wave mixing (DFWM) measurements reveal unusually large optical nonlinearity: $\chi^{(3)}$ values as high as 4.5×10^{-9} esu for polymer (a), an open chain version of triphenodioxazine, have been observed.

The reaction of (1) and chloranil to synthesize the prepolymer (see reaction 1) can be carried out in several different solvents. The prepolymer so obtained is only partially soluble in DMF and insoluble in ethanol, pyridine, acetone and chloroform, which likely reflects the effect of hydrogen bonding in the prepolymer.

$$
\text{(1)} + n \, \text{(chloranil)} \xrightarrow[\text{DMF}]{K_2CO_3}
$$

(1)

··········· Reaction 1

prepolymer
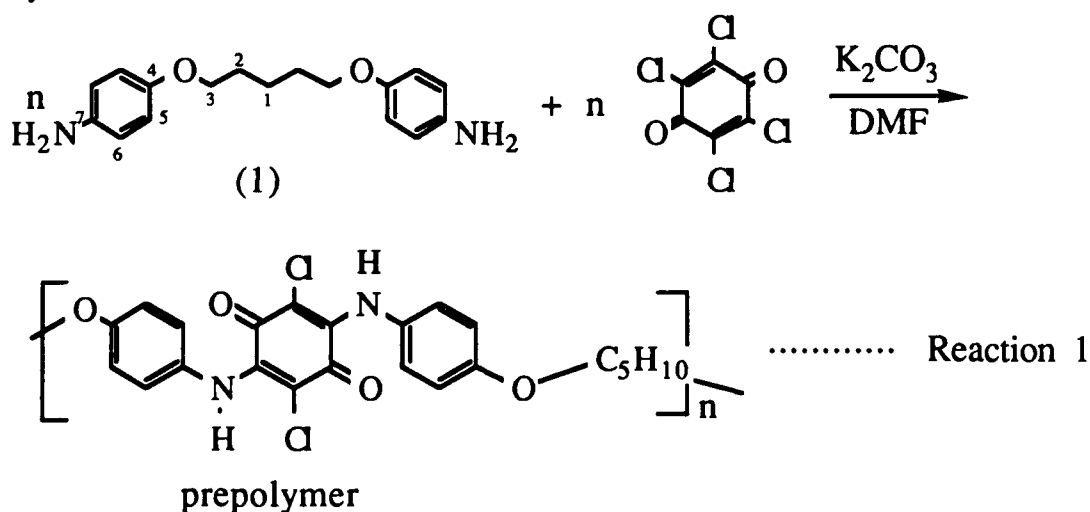
The formation of triphenodioxazine from 2,4-diarylamine-3,5-dichloroquinone (2) is via a Friedel-Crafts reaction. The reaction was carried out in nitrobenzene with benzoyl chloride as the catalyst (reaction 2). The color of the mixture changed from brown to red, which is the characteristic color of triphenodioxazine. The final polymer is soluble in DMF and 1-chloronaphthalene. Spectroscopic studies and elemental analysis indicate that

the polymer is an open chain copolymer, as shown in reaction 2, instead of cyclized triphenodioxazine copolymer.

Prepolymer $\xrightarrow[\text{Benzoyl chloride}]{\text{Nitrobenzene}}$

polymer (a)

.... Reaction 2
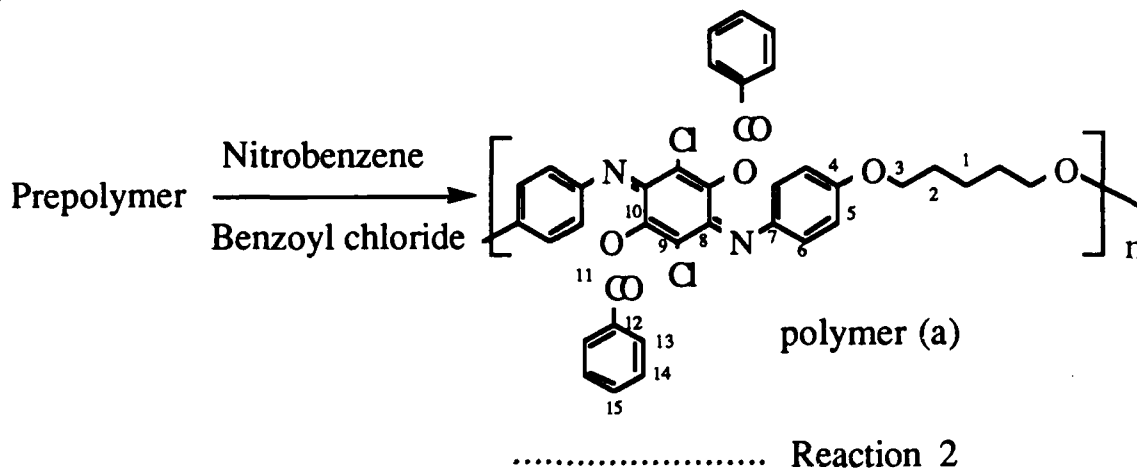
Although polymer (a) is not fully cyclized triphenodioxazine copolymer, it has these advantages: it is fully soluble in DMF, DMSO, and 1-chloronaphthalene; and optical quality films can be cast from the solutions. GPC measurements in DMF show that the molecular weight of polymer (a), MW, is about 22600 using polystyrene as the standard.

Polymer (a) is thermally stable up to 480°C, except for a small percentage (2%), of weight loss at 330°C, which might be caused by some impurities. DSC shows a T_g transition at 170°C and a T_m transition around 250°C.

To get a fully cyclized copolymer, we tried different reaction methods. Since it is well known that this cyclization is an oxidative ring closure process, we think that the reaction could be promoted by the addition of oxidative agents. Thus, when we add a small amount of iodine (1%) to the nitrobenzene and benzoyl chloride reaction media, the rate of reaction is accelerated. Only one hour is needed to complete the reaction, but the structure of the final polymer is the same as that of polymer (a). P_2O_5 and PCl_5 have been tested as catalysts in nitrobenzene and dichlorobenzene, but the final products are intractable black solids. However, when we use p-toluene sulfonyl chloride as the catalyst in 1-chloronaphthalene, cyclization occurs.

Prepolymer $\xrightarrow{\text{TsCl, C}_8\text{H}_7\text{Cl}}$
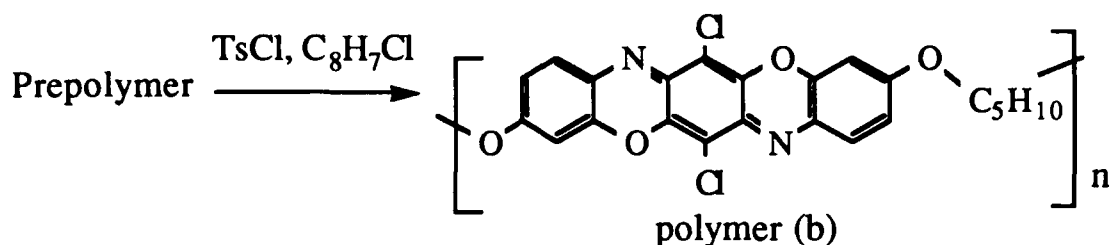
polymer (b)

.... Reaction 3

Polymer (b) is soluble in 1-chloronaphthalene and partially soluble in DMF. The FTIR spectrum of polymer (b) (Fig. 7) is similar to that of the model compound and shows a marked change from that of polymer (a). The carbonyl absorption at 1775 cm^{-1} in polymer (a) is absent in polymer (b). The peak due to >C=N- appears at 1627 cm^{-1} and the out-of-plane deformation peaks due to aromatic protons have changed from the 1,4-substituted pattern (831 cm^{-1}) of the prepolymer and polymer (a) to the 1,2,4-substituted pattern (773, 826, 872 cm^{-1}) of polymer (b). Elemental analysis shows a discrepency between the theoretical and experimental values. This can be reconciled by assuming that the final polymer structure is not as perfect as we expected. Some side reaction might have accompanied the cyclization reaction. The following polymer structure gives a very good fit of elemental analysis data.
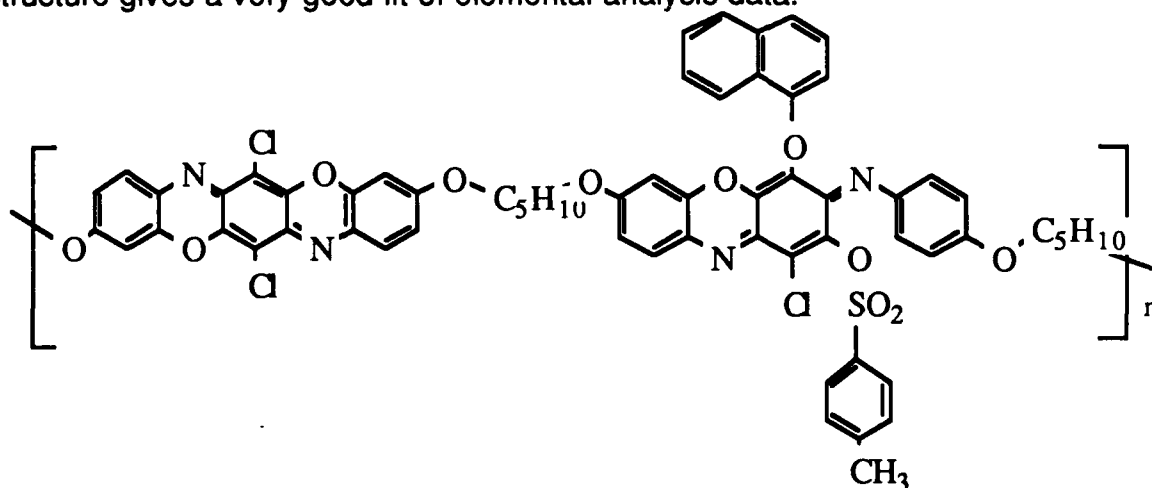
Best fit structure for polymer (b)

The UV/Vis spectrum of polymer (a) is identical with that of the model compound. Three peaks in the visible region (478.5, 515, 566.5 nm) can be observed. Both polymer (a) and polymer (b) show sharp-defined optical absorption band-edges. This is an advantage for NLO studies, since one can more easily determine the nonresonant contribution to the NLO process.

TGA studies indicate that polymer (b) is thermally stable up to 360°C It was realized that this polymer had the potential to exhibit liquid crystallinity. However, DSC shows that no thermal process occurs below 300°C. Since this may reflect the length of the flexible chain spacers groups, synthesis of copolymer with longer spacers is in progress..

GPC study of the soluble portion of polymer (b) in DMF shows a multipeak distribution pattern with MW varying from 25500 to 84300. Since we use polystyrene as standard, these values seem to be overestimated according to the film quality of this polymer.

DFWM measurements have been performed on both polymer (a) and polymer (b), which are cast on glass plates. Film from polymer (b) has a large light scattering because the polymer is easy to aggregate when films are prepared due to limited solubility. This results in a DFWM signal for polymer (b) with a large amount of noise. Accurate results are yet to be determined and will be reported separately. According to our current observation, polymer (a) and polymer (b) have similar NLO behavior.

The results of our study of the NLO properties of a rigid rod/flexible chain copolymer clearly show that it is possible to improve the processibility of existing conjugated polymers without sacrificing optical nonlinearity, as is consistent with theoretical prediction. It is important to note from this work that incorpration of some dye molecules into a polymer backbone is an appropriate research direction to pursue in order to promote the third order NLO properties of polymeric materials.

A Study of the Electronic Properties of the Ladder Polymers BBB and BBL.

In collaboration with Dan Davidov[44] and co-workers, we are investigating the electronic properties of heteroaromatic ladder polymers of the benzoimidazobenzophenanthroline type, BBB and BBL. Historically, these polymers have been examined as high performance (excellent mechanical and thermal stabilities) polymers for use in advanced aerospace textile applications[45,46]. However, the presence of extended π-conjugation, leading to mobile delocalized π-electrons in such rigid rod polymers, prompted us to investigate their electronic properties, particularly with respect to their use as third order nonlinear optical materials. Both BBB and BBL, in common with other conjugated polymers, are capable of supporting mobile bond alternation defects such as solitons, polarons and bipolarons which are expected to play a

role as the charge carriers in mechanisms involved in the third order nonlinear optical (NLO) response. In addition, chemical or electrochemical doping leads to a change in physical properties, particularly noticeable as a large increase in conductivity. It is our intention to correlate such changes with changes in the NLO response by the use of techniques such as electron spin resonance (ESR) and conductivity and optical (bandgap) measurements, coupled with a degenerate four wave mixing (DFWM) technique to measure the third order NLO susceptibility $\chi^{(3)}$.

ESR measurements and analysis

ESR measurements were performed on pristine and thermally annealed thin (20 microns) films of BBB and BBL.[47] Both polymers gave a strongly anisotropic signal, suggesting a highly planar polymer backbone. The ESR data implies the existence of two different types of spin species. Thermally annealing the BBB and BBL films to high temperatures, T_0, increases the spin susceptibility for $T_0 < 850K$. However, annealing to $T_0 > 900K$ results in a dramatic reduction in the spin susceptibility and a dramatic increase in the conductivity.[48] In fact, the room temperature in-plane conductivity of annealed samples (900K) exceeds $\sigma = 1 \ \Omega^{-1} \ cm^{-1}$. We believe this to be due to a phase transition to a fully condensed, cross-linked aromatic structure.

The spin concentration can also be increased through photogeneration at various excitation wavelengths.[49] The results imply long-lived localized photogenerated polarons whose lifetime can be described by a two-component exponential decay function. The two different decay processes may be explained as interchain and intrachain recombination of the localized polarons. Their lifetime dramatically increases with decreasing temperature and strongly depends on the wavelength of the exciting radiation. The similarities in the ESR properties for the photogenerated, thermally generated and native spins indicates that the spin species all exhibit polaronic character. Third order NLO studies are underway to correlate NLO properties to concentration of spins.

Thermal Annealing and Doping

Current studies indicate that exposure of heat treated BBB and BBL polymers to fluorine results in transparent and stable polymers with enhanced conductivities[50]. This is of interest because undoped ladder polymers are not attractive for device application due to their large light absorbance, particularly

in the visible region. The polymers were flourinated at room temperature at about 100 torr F_2; weight increase measurements indicate a weight uptake of approximately 22 (BBB) and 16 (BBL) fluorine atoms per monomer unit. Such treatment shifts the absorption edge from 2 eV in pristine BBL to 3.4 eV for flourinated BBL. By careful thermal annealing before doping, it is possible to produce stable, transparent and somewhat conducting polymers that are still partially conjugated. It is also possible to utilize laser annealing as a spatially selective heating technique, resulting in conducting patterns in an insulating BBB or BBL polymer matrix. Subsequent fluorination leads to conducting patterns embedded in a completely transparent polymer.

Third Order NLO Studies of 7-Nitrobenzo-2-oxa-1,3-diazole (NBD)

The second order NLO properties of NBD chloride are currently receiving a great deal of interest in the scientific community.[51] We are interested in determining whether or not NBD has third order NLO properties, and preliminary results on attachment of nucleophilic and electrophilic dyes (including NBD) to polymeric backbones has recently been reported by our research group (Scheme 9).[52]

It is interesting to investigate the morphological dependencies on the NLO behavior comparing composite films of NBD in a polymeric matrix (randomly distributed) to polymer films with NBD groups directly attached to the polymeric backbone. To achieve this, a series of styrene copolymers with varying amounts of p-aminostyrene were prepared with NBD attached, and the NLO properties of these systems compared with composite films prepared by incorporating NBD into a polycarbonate matrix.

On attachment of the NBD chloride to the p-aminostyrene copolymer support, the substituent at carbon number 2 in the dye moiety changes from chlorine to amino. In order to test whether the dye had changed significantly upon attachment and whether this new species was giving rise to the NLO behavior, model compounds were prepared (Figure 10). We are in the process of comparing spectral data of these model compounds with our copolymeric systems.
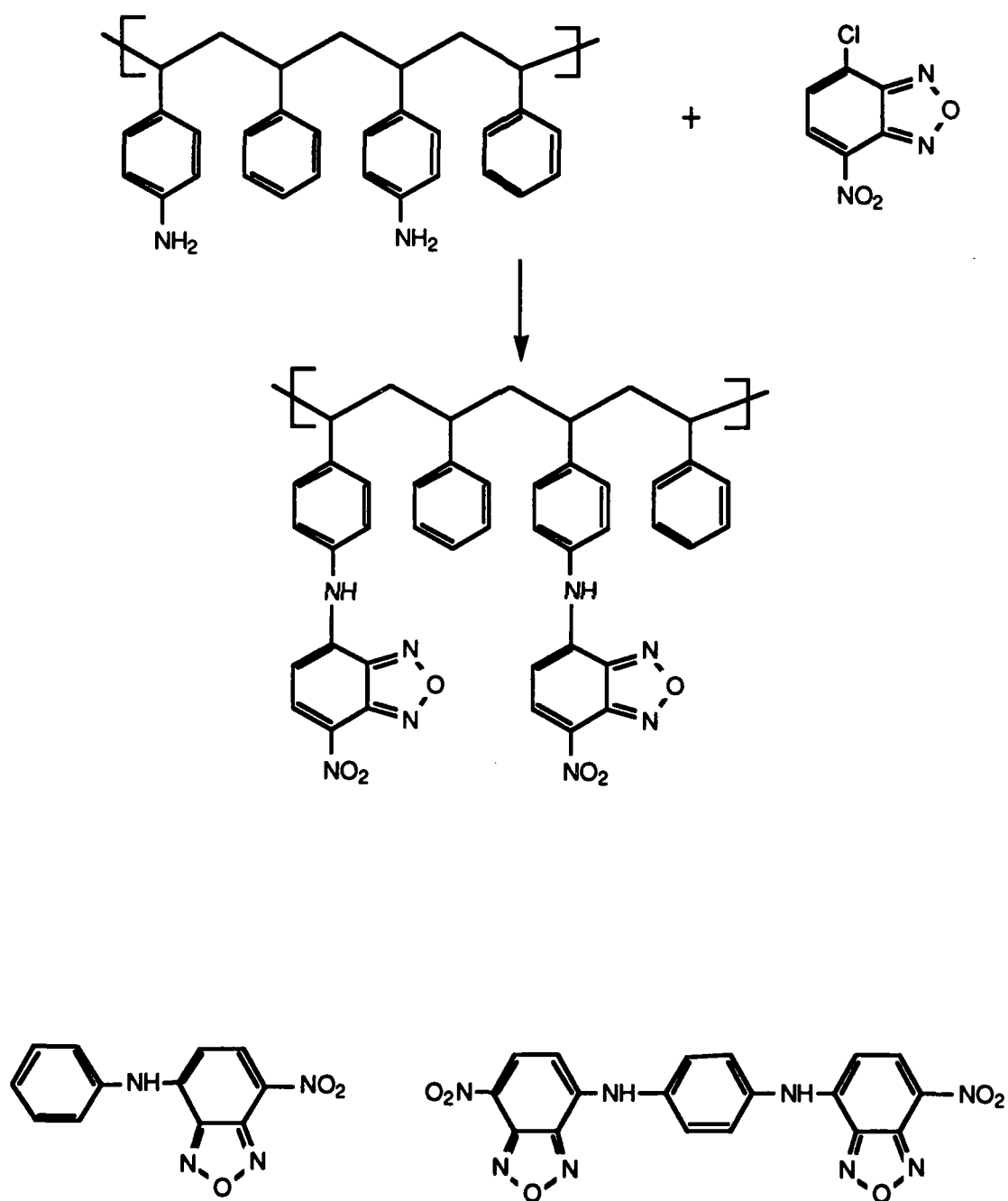
Scheme 9

Figure 10. Model Compounds for the 7-nitrobenzo-2-oxa-1,3-diazole (NBD)

Preliminary degenerate four wave mixing results for all materials indicate that the copolymeric support allowed incorporation of greater amounts of

electroactive units, versus composites, and hence allowed high third order nonlinear responses ($\chi^{(3)}/\alpha$ of approximately 10^{-13} esu cm) (Table V). Third order NLO responses were absent in composite systems due to limited solubility and/or phase separation difficulties.

Table V. Third Order Susceptibilities for Systems Studied

Polymer support	$\chi^{(3)}/\alpha^a$
Polycarbonate[b]	not measurable.
5 % p-aminostyrene	not measurable
10 % p-aminostyrene	0.55 X 10^{-13}
20 % p-aminostyrene	0.72 X 10^{-13}
66 and 75 % p-aminostyrene	---c

a) in units of e.s.u. cm   b) Nominal 5 to 10% dye incorporation
c) insoluble

At low incorporation (5 molar percent) the copolymeric and composite systems showed no measurable NLO response. It was not possible to incorporate more that 10% of NBD into composites due to phase separation problems, however, copolymeric incorporation at 20 and 30 molar percent yielded materials which gave a third order NLO signal which, within the error of the measurement , remained relatively small and constant. At very high incorporation of NBD, 66 and 75 molar percent, insolubility of the copolymer resulted.

It is clear from these studies that limitations due to phase separation may be a key deficiency in the utilization of composite systems for third order NLO effects. By the facile procedure of attaching dyes to polymeric supports, we not only increase the concentration of the dye to higher levels not achievable in composite systems, but phase separation problems are avoided.

We are now expanding this study to better understand the morphological dependencies which give rise to the NLO phenomenon by designing new dye molecules that can be attached to electrophilic polymers (i.e., copoly(styrene-p-chloromethystyrenes).

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